

# Positional Order and Diffusion Processes in Particle Systems

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Nonequilibrium behaviors of positional order are discussed based on diffusion processes in particle systems. With the cumulant expansion method up to the second order, we obtain a relation between the positional order parameter  $\Psi$  and the mean square displacement  $M$  to be  $\Psi \sim \exp(-\mathbf{K}^2 M/2d)$  with a reciprocal vector  $\mathbf{K}$  and the dimension of the system  $d$ . On the basis of the relation, the behavior of positional order is predicted to be  $\Psi \sim \exp(-\mathbf{K}^2 Dt)$  when the system involves normal diffusion with a diffusion constant  $D$ . We also find that a diffusion process with swapping positions of particles contributes to higher orders of the cumulants. The swapping diffusion allows particle to diffuse without destroying the positional order while the normal diffusion destroys it.

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The melting behavior of the hard-disk system was reported first by Alder *et al.* [1], and they showed that only repulsive interactions can involve the melting transition. This melting transition also confirmed in three-dimensional systems and is now often referred to Alder transition. However, Mermin ruled out the positional long range order in two-dimensional particle systems [2]. Therefore, the melting processes of two-dimensional systems are different from that of three-dimensional systems. Halperin, Nelson, and Young proposed the two-dimensional melting theory [3] based on Kosterlitz Thouless transition [4], and Chui proposed another theory predicting the first order transition based on the grain boundaries excitation [5]. While many researchers have been studying this problem [6, 7, 8, 9, 10, 11], the nature of two-dimensional melting has been still a matter of debate [12]. So far, most of numerical works have focused on the equilibrium state of the system mainly using Monte Carlo methods. Recently, the nonequilibrium behaviors of the bond-orientational order parameters has been studied to obtain the equilibrium properties of the hard-disk systems [13]. These studies are based on a new strategy for the simulation, called Non-equilibrium relaxation (NER) method [14]. Zahn and Maret studied time dependent parameters in two-dimensional colloidal particle systems [15]. They pointed out that static properties are not appropriate measure to distinguish between the solid and the fluid, since the mean square displacement diverges very slowly. Therefore, it is necessarily to study the dynamic behaviors of order parameters in the particle systems. In this letter, we study the dynamics of the positional order parameter based on diffusion processes. We also treat two- and three-dimensional systems at the same time, since many studies have focused only on the

two-dimensional melting and, to our knowledge, there are less studies about the three-dimensional positional order.

Consider a  $d$ -dimensional system with  $N$  particles. A positional order parameter  $\Psi$  of the system is defined to be

$$\Psi = \frac{1}{N} \sum_j^N \exp(-i\mathbf{K} \cdot \mathbf{r}_j), \quad (1)$$

with the position of the particles  $\mathbf{r}_i$  and one of the reciprocal vectors  $\mathbf{K}$  of the system. Let  $\mathbf{R}_i$  be the equilibrium position of the particle  $i$  and  $\mathbf{u}_i$  the deviations from it, namely,  $\mathbf{r}_i = \mathbf{R}_i + \mathbf{u}_i$ . The positional parameter is reduced to be,

$$\Psi = \langle \exp(-i\mathbf{K} \cdot \mathbf{u}_j) \rangle, \quad (2)$$

where  $\langle \cdots \rangle$  means the average for all particles. Assuming that the all components of  $\mathbf{u}_i$  have the Gaussian distribution, Eq. (2) is reduced to be [17],

$$\Psi = \exp(-1/2 \langle (\mathbf{K} \cdot \mathbf{u}_i)^2 \rangle). \quad (3)$$

Assuming that  $\mathbf{u}_i$  is isotropic, we have,

$$\langle (\mathbf{K} \cdot \mathbf{u}_i)^2 \rangle = K^2 \langle \mathbf{u}_i^2 \rangle / d \quad (K \equiv |\mathbf{K}|). \quad (4)$$

From Eqs. (3) and (4), we obtain the relation between the positional order and the diffusion to be, positional order parameter to be,

$$\Psi = \exp\left(-\frac{K^2 \langle \mathbf{u}_i^2 \rangle}{2d}\right), \quad (5)$$

or equivalently,

$$\langle \mathbf{u}_i^2 \rangle = -\frac{2d}{K^2} \ln \Psi. \quad (6)$$

Note that, the above argument is the cumulant expansion. The positional order parameter is the characteristic

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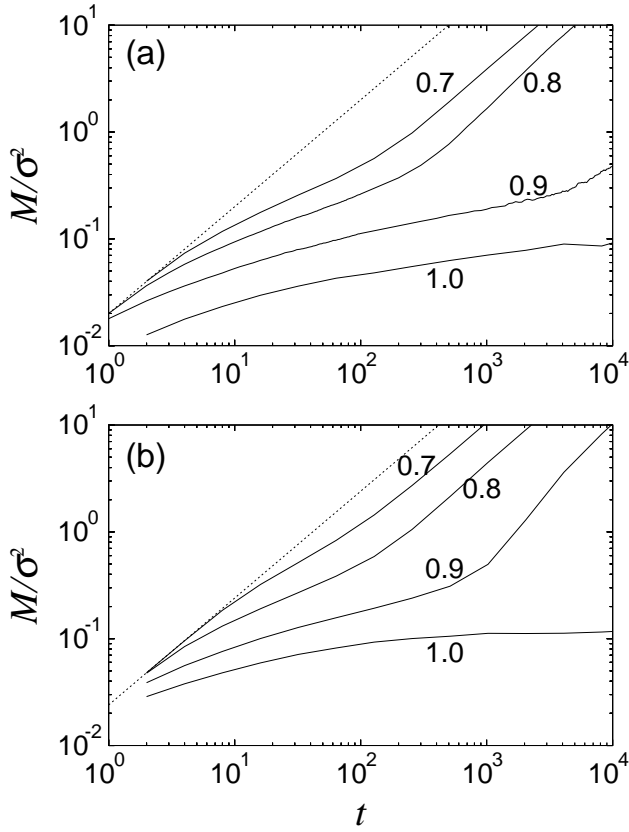


FIG. 1: Time evolution of the mean square displacement  $M \equiv \langle u_i^2 \rangle$  in (a) two- and (b) three-dimensional systems. The decimal logarithm are taken for the both axes. The dashed lines denote the diffusion in the low density limit [16]. Number of particles  $N = 23288$  for two- and  $N = 36000$  for three-dimensional system with the periodic boundary condition.

function of displacements. Assuming the distribution of the displacement to be the Gaussian distribution, we can express the positional order parameter only with the second order cumulant, which is diffusion.

When a system involves the normal diffusion, the asymptotic behavior of the mean square displacement is expected to be,

$$\langle \mathbf{u}_i^2 \rangle \sim 2dDt, \quad (7)$$

with a diffusion constant  $D$ . From Eqs. (5) and (7), the asymptotic behavior of the positional order to be,

$$\Psi(t) \sim \exp(-K^2Dt), \quad (8)$$

regardless of the dimension. It implies that when the system involves the normal diffusion, the positional order should decay exponentially with the decay time  $D^{-1}$ . This limits the diffusion behavior in solid phases. In the solid phase of the system with  $d \geq 3$ , the parameter  $\Psi$  has non-zero value in the equilibrium state. Therefore, the mean displacement cannot become larger than some constant value. The behavior in two-dimensional solid is different from those in  $d \geq 3$ . On the basis of the

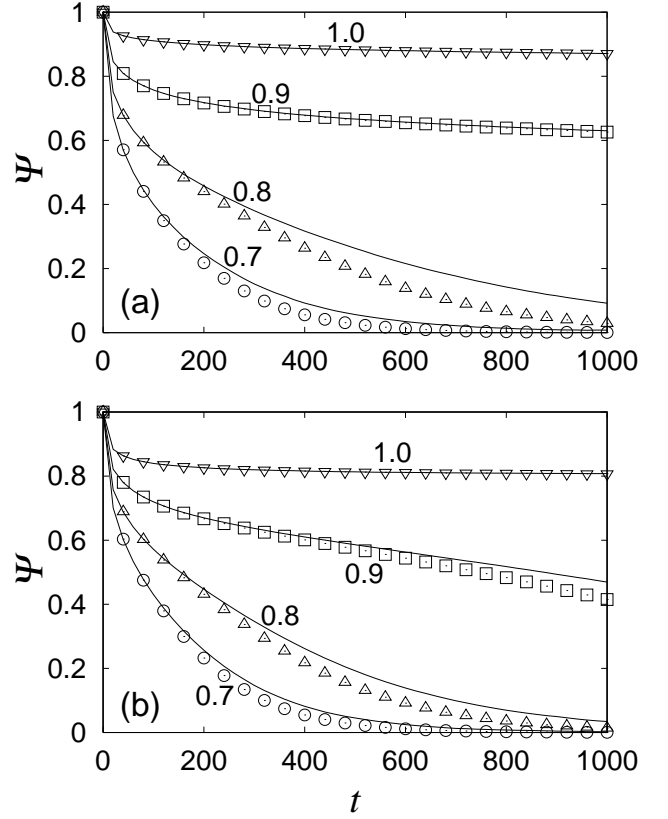


FIG. 2: Time evolution of the positional order parameter and calculated values from the diffusion for (a) two- and (b) three-dimensional systems. The solid lines are the positional order parameters and the symbols are the calculated values using Eq. (5). It shows good agreement in the region where the positional order parameters are not so small.

Halperin-Nelson-Young theory [3], the positional order parameter in two-dimensional solid behaves as,

$$\Psi(t) \sim t^{-\lambda}. \quad (9)$$

The mean square displacement in two-dimensional solid behaves logarithmically as,

$$\langle \mathbf{u}_i^2 \rangle = \frac{4\lambda}{K^2 z} \ln t. \quad (10)$$

Therefore, two-dimensional solid cannot involve the normal diffusion process in the usual sense.

The above arguments are based on the cumulant expansion up to the second order. In order to check the validity of our arguments, we perform numerical simulations. For the simplicity, we treat the hard-particle systems. There are two kinds of methods to study time evolution of a particle system, a molecular dynamics (MD) method and a Monte Carlo (MC) method. The MD simulation is performed by integrating the classical equations of motion. In the hard particle system, the time evolution is performed by proceeding collision events. This algorithm is called the Event-Driven method, which is very

efficient to treat the hard-particle system [18, 19, 20]. When the time evolution of the system is performed by MD, however, the positional order has oscillations because of the momentum conservation. This oscillation prevents us from studying the order parameter, therefore, MC simulations are performed in this study.

Each system contains  $N$  particles with the radius  $\sigma$ . The density is normalized to be  $\rho = 1$  when the system is in the perfect square/cubic lattice, that is,  $\rho \equiv (2d/L)^d N$  with the dimension of the system  $d$  and the linear size of the system  $L$ . Throughout this study, the number of particles  $N = 23288$  for two- and  $N = 32000$  for three-dimensional systems and up to 512 independent samples are averaged for each density. The step length is set to be  $\sigma_s = 0.2\sigma$  with the radius  $\sigma$  [21]. At the beginning of each run, the particles are set up in the perfect ordered configuration, namely, the hexagonal lattice in the two-dimensional and the face centered cubic lattice. The periodic boundary conditions are taken along the all axes. The densities from  $\rho = 0.7$  to 1.0 are studied.

The time evolutions of the mean square displacements  $M$  are shown in Fig. 1. We can see the normal diffusions starting after some initial relaxations, for example, the data of three-dimensional system with  $\rho = 0.9$  has a bend at  $t \sim 10^3$ . It implies that the normal diffusion started after the positional order are almost destroyed. The time evolutions of the positional order parameters are shown in Fig. 2. While the positional order is well approximated by the second order cumulant in the region where the positional order parameter is not so small, there are differences especially in the low densities.

These differences are caused by the higher order cumulants which are ignored in Eq. (3). The contribution from the higher order cumulants can be explained by a swapping diffusion process. In particle systems, there are two kinds of ways to diffuse; by normal diffusion and the swapping. While the normal diffusion destroys the positional order parameters as described in Eq. (5), the swapping does not. In Fig. 3, the diffusion behavior in two-dimensional solid is shown. The density is  $\rho = 0.92$  which is high enough than the melting points  $\rho_m$ , *i.e.*,  $\rho_m \sim 0.902$  reported by Zollweg and Chester [6] and  $\rho_m < 0.905$  by Weber *et al.* [8], and  $\rho_m \sim 0.893$  by Watanabe *et al.* [13]. The diffusion shows logarithmic behavior up to  $t \sim 10^4$  as Mermin predicted [2]. However, it varies from the logarithmic behavior because of the swapping diffusion around at  $t \sim 10^5$ . The distribution of the displacement  $\mathbf{u}_i$  at this time is shown in Fig. 4. The points around at the center correspond to the results of the normal diffusion and the six groups around the center group correspond to that of the swapping diffusion.

In order to treat the effect of the swapping, we consider the system with two types of diffusion, the continuous diffusion and the swapping diffusion with a swapping rate  $E_r$  on the lattice with a lattice constant  $a$ . The rate  $E_r$  denotes the probability to jump to the nearest position at equilibrium per unit time. The diffusion with swapping

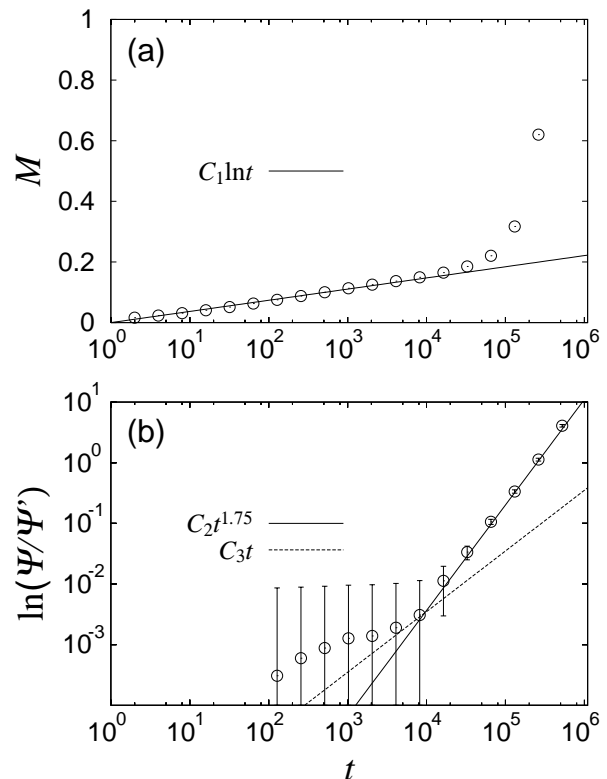


FIG. 3: (a) Mean square displacement  $M$  of the two-dimensional solid. The number of particles  $N = 23288$  and the density  $\rho = 0.92$ . The solid line is  $C_1 \ln t$  with  $C_1 = 1.6 \cdot 10^{-2}$ . Error bars are smaller than the size of the symbols. It shows that the crossover from the normal diffusion (logarithmic) to the swapping diffusion (power-law). (b) The time evolution of the value  $\ln(\Psi/\Psi')$ , where  $\Psi$  is the positional order parameter with the definition in Eq. (1) and  $\Psi'$  is the value calculated from diffusion using Eq. (5). The decimal logarithms are taken for the both axes. The solid and dashed lines are drawn for the guides to the eyes; The solid line is  $C_2 t^{1.75}$  and the dashed line is  $C_3 t$  with  $C_2 = 4.0 \cdot 10^{-10}$  and  $C_3 = 3.5 \cdot 10^{-7}$ . It shows that the exchanging rate increases as  $E_r \sim t^{0.75}$ .

$\langle \mathbf{u}_i^2 \rangle'$  is expressed to be,

$$\langle \mathbf{u}_i^2 \rangle' = \langle \mathbf{u}_i^2 \rangle + da^2 E_r t, \quad (11)$$

with the diffusion without swapping  $\langle \mathbf{u}_i^2 \rangle$  [22]. In the following, the positional order parameter calculated from Eq. (5) is denoted by  $\Psi'$  in order to distinguish from the original definition in Eq. (1). Using  $E_r$ ,  $\Psi'$  can be expressed to be,

$$\begin{aligned} \Psi' &= \exp \left( -\frac{K^2 \langle \mathbf{u}_i^2 \rangle'}{2d} \right) \\ &= \Psi \exp (-2\pi^2 E_r t). \end{aligned} \quad (12)$$

Therefore,  $\Psi'$  is always smaller than  $\Psi$ , since  $E_r > 0$ . The contribution of the higher order cumulants is ex-

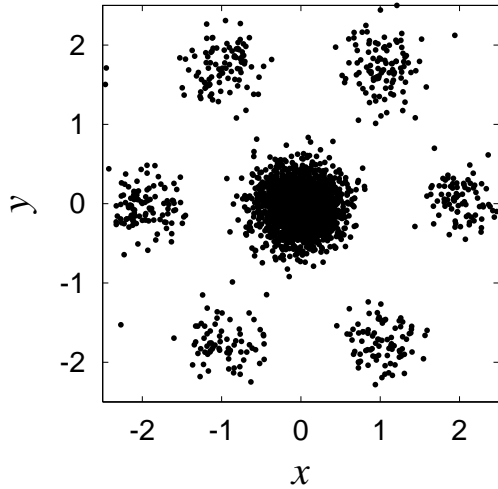


FIG. 4: Distribution of displacements  $\mathbf{u}_i$  at  $t = 5 \cdot 10^5$  of the two-dimensional system. A small system with  $N = 2900$  is shown for visibility. The density of the system is  $\rho = 0.92$ . The lattice constant is  $a = 2$  and the radius of particles is  $\sigma = 0.89$  in this scale. The center  $(0,0)$  corresponds to the initial position  $\mathbf{R}_i$ . The points around at the center correspond to the normal diffusion and the six small groups around the center group correspond to the swapping diffusion.

pressed to be,

$$\ln(\Psi/\Psi') = 2\pi^2 E_r t. \quad (13)$$

The time evolution of the value  $\ln(\Psi/\Psi')$  is shown in

Fig. 3(b). It increases as  $\sim t^{1.75}$ , which is faster than linear increase. If the exchanging rate  $E_r$  is constant, the value should increase as  $\sim t$ . Therefore, the exchanging rate  $E_r$  increases. It implies that the destruction of the positional order enhances the swapping of the particles.

To summarize, we study the dynamics of the positional order in the particle systems based on the diffusion processes. We discuss the relation between the positional order parameter  $\Psi$  and the mean square displacement  $M$  with the cumulant expansion. We find that there are two kinds of diffusion processes in particle systems, one is the normal diffusion and another is the swapping diffusion which allows particles to diffuse without destroying the positional order. These diffusion processes can be understood as cumulants of the displacements; the normal diffusion is the second order cumulant, and the swapping diffusion contributes to the higher orders. This swapping diffusion process will play important roles in systems with two or more kinds of particles in high density region. The presented arguments are very general, and applicable to other systems with general pair potentials. Studying dynamic aspects of Alder transitions based on the cumulant expansion should be a further issue.

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  - [22] Consider a diffusion process on the grid with the lattice constant  $a$ . If particles jump randomly to the next site every  $\tau$ , the system involves diffusion with a diffusion constant  $D = a^2 / 2\tau$  and the exchanging rate  $E_r$  is denoted by  $E_r = \tau^{-1}$ .